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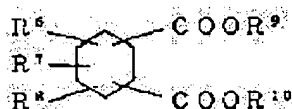
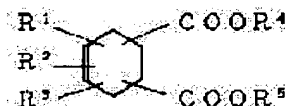
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NOBE TOMIO**(54) POLYOLEFINIC RESIN COMPOSITION**

(57)Abstract:

PURPOSE: To obtain a resin composition excellent in fluidity, processability, cold resistance, etc., and useful as a molding material by blending a polypropylene-based resin and/or a polyolefinic thermoplastic elastomer with a specific alicyclic dicarboxylic acid ester.

CONSTITUTION: This resin composition is obtained by blending (A) 100 pts.wt. of a polypropylene-based resin and/or a polyolefinic thermoplastic elastomer with (B) 0.2-60 pts.wt., preferably 0.2-35 pts.wt. of one or two or more alicyclic dicarboxylic acid esters of formula I (R1, R2 and R3 are H, a 1-5C alkyl, 2-5C alkenyl or endomethylene; R4 and R5 are a 6-28C alkyl or alkenyl) or formula II (R6, R7 and R8 are H, a 1-5C alkyl, 2-5C alkenyl or endomethylene; R9 and R10 are a 6-28C alkyl or alkenyl).



II

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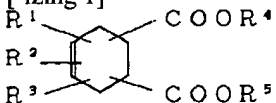
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CLAIMS

[Claim]

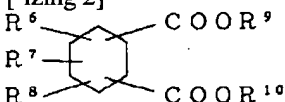
[Claim 1] The polyolefine system resin constituent characterized by coming to blend one sort expressed with a general formula (1) or a general formula (2), or two sorts or more of alicyclic dicarboxylic-acid ester to a polypropylene resin and/or polyolefine system thermoplastic elastomer.

[-izing 1]



the inside of [formula, and R^1 , R^2 and R^3 -- an identity -- or -- differing -- a hydrogen atom, the shape of a straight chain of carbon numbers 1-5, a branched-chain alkyl group, the shape of a straight chain of carbon numbers 2-5, and a branched-chain alkenyl machine -- or -- and a methylene group is expressed R^4 and R^5 -- an identity -- or it differs and the shape of a straight chain, the branched-chain alkyl group, or alkenyl machine of carbon numbers 6-28 is expressed]

[-izing 2]



the inside of [formula, and R^6 , R^7 and R^8 -- an identity -- or -- differing -- a hydrogen atom, the shape of a straight chain of carbon numbers 1-5, a branched-chain alkyl group, the shape of a straight chain of carbon numbers 2-5, and a branched-chain alkenyl machine -- or -- and a methylene group is expressed R^9 and R^{10} -- an identity -- or it differs and the shape of a straight chain, the branched-chain alkyl group, or alkenyl machine of carbon numbers 6-28 is expressed]

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DETAILED DESCRIPTION

[Detailed description]

[0001]

[Field of the Invention] this invention relates to a polyolefine system resin constituent useful as a molding material.

[0002] A polypropylene resin, polyolefine system thermoplastic elastomer, and those mixture are known as a material useful for various intended use, such as an injection-molding article, a film, a flat yarn, fiber, a blow-molding article, and an extrusion-molding article.

[0003] Since the shock resistance in low temperature and flexibility were low, the polypropylene resin had the inclination to receive a limit in the use especially in a cold district, and since the concerned resin had a low fluidity, when bulking agents, such as a flame retarder, and a calcium carbonate, a glass fiber, were blended and processed, it had the problem that a moldability was inferior.

[0004] Although polyolefine system thermoplastic elastomer has shock resistance and good flexibility, since a property like a polyvinyl chloride resin system elastomer or a soft polyvinylchloride resin is not provided, in spite of the room of an improvement having accepted, in addition, the improvement means effective until now is not especially known as a material in the intended use of inner sheathing, such as an automobile and a vehicle, electrical wire and a household-electric-appliances device, engineering works, construction and building materials, a hose tube, etc.

[0005]

[Object of the Invention] The fluidity and the workability of a resin are improved and the shock resistance (cold resistance) in low temperature and flexibility aim this invention at offering a good polyolefine system resin constituent.

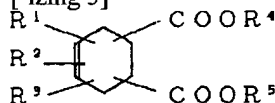
[0006]

[The means for solving a technical problem] In order that this invention persons may attain the above-mentioned purpose, zealously, to a polypropylene resin, polyolefine system thermoplastic elastomer, or those mixture, by blending the ester compound which has specific structure, they find out that a desired effect is acquired and came to complete this invention based on such knowledge as a result of the study.

[0007] That is, it is characterized by the polyolefine system resin constituent concerning this invention coming to blend one sort expressed with a general formula (1) or a general formula (2), or two sorts or more of alicyclic dicarboxylic-acid ester (for it to be named "this ester" generically below.) to a polypropylene resin and/or polyolefine system thermoplastic elastomer (it being named "this resinous principle" generically below.).

[0008]

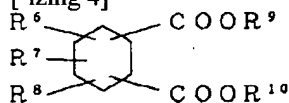
[Chemical structure 3]



the inside of [formula, and R1, R2 and R3 -- an identity -- or -- differing -- a hydrogen atom, the shape of a straight chain of carbon numbers 1-5, a branched-chain alkyl group, the shape of a straight chain of carbon numbers 2-5, and a branched-chain alkenyl machine -- or -- and a methylene group is expressed R4 and R5 -- an identity -- or it differs and the shape of a straight chain, the branched-chain alkyl group, or alkenyl machine of carbon numbers 6-28 is expressed]

[0009]

[Chemical structure 4]



the inside of [formula, and R6, R7 and R8 -- an identity -- or -- differing -- a hydrogen atom, the shape of a straight chain of carbon numbers 1-5, a branched-chain alkyl group, the shape of a straight chain of carbon numbers 2-5, and a branched-chain alkenyl machine -- or -- and a methylene group is expressed R9 and R10 -- an identity -- or it differs and the shape of a straight chain, the branched-chain alkyl group, or alkenyl machine of carbon numbers 6-28 is expressed]

[0010] Although especially the manufacture technique of this ester is not limited and well-known arbitrary operations can be

conventionally used for it, the method of esterifying a predetermined dicarboxylic acid, or the acid anhydride and a predetermined fatty alcohol as the general technique, while removing produced water under presence of a non-catalyst or a catalyst is mentioned.

[0011] The ester expressed with a general formula (1) is easily compounded by carrying out the esterification reaction of an alicyclic unsaturation dicarboxylic acid, or its predetermined anhydride and predetermined fatty alcohol according to a conventional method.

[0012] As the concerned alicyclic unsaturation dicarboxylic acid or its anhydride, the acid anhydride obtained by the reaction of deca trien, such as a tetrahydrophthalic acid, a methyl tetrahydrophthalic acid, a dimethyl butenyl tetrahydrophthalic acid, a ***** acid, a methyl ***** acid, methyl highness *****s, those anhydrides and those isomers (a geometrical isomer and a structural isomer are included.), and ******, alpha-terpinene, and a maleic anhydride, its disengagement carboxylic acid, etc. are illustrated.

[0013] The ester expressed with a general formula (2) is easily compounded by carrying out the esterification reaction of an alicyclic saturation dicarboxylic acid, or its predetermined acid anhydride and predetermined fatty alcohol according to a conventional method. Moreover, it can obtain also by carrying out nuclear hydrogenation of the ester expressed with a general formula (1).

[0014] As the concerned alicyclic saturation dicarboxylic acid or its anhydride, hexahydrophthalic acid, methyl hexahydrophthalic acid, ***** acid hydrogenation object, methyl ***** acid hydrogenation object, 1, and 4-cyclohexane dicarboxylic acids, these acid anhydrides, those isomers (a geometrical isomer is included.), etc. are illustrated.

[0015] The fatty alcohol used as an alcoholic component of each above-mentioned ester concerning this invention is a fatty alcohol of the saturation of carbon numbers 6-28, or an unsaturation, and is a fatty alcohol of carbon numbers 8-24 more preferably. Since the compatibility to a polyolefine system resin falls in less than six alcohol, and it is easy to carry out bleeding of the carbon number, and the molecular weight of ester becomes small and oil resistance falls in the alcohol in which a volatility-proof is inferior with alcohol and a carbon number exceeds 28 conversely, it is not desirable.

[0016] As a desirable fatty alcohol concerning this invention A heptanol, 2-ethyl hexanol, n-octanol, iso nonanol, A 3, 5, and 5-trimethyl hexanol, n-decanol, an iso decanol, An undeca Norian, a dodecanol, a tridecyl alcohol, ***** 610 (vista chemical Far East company make), ***** 79 -- said -- 911 (shell chemistry company make) and gold [a diamond / 79] -- said -- 911 -- said -- 11 -- said -- 113 (Mitsubishi Kasei Corp. make) -- The dimerization alcohol obtained by the gar bed reaction of a myristyl alcohol, cetyl alcohol, a stearyl alcohol, a behenyl alcohol, oleyl alcohol, and these alcohol is illustrated.

[0017] As an esterification catalyst chosen and applied in the above-mentioned esterification A sulfuric acid, a hydrochloric acid, a phosphoric acid, Para toluenesulfonic acid, a methanesulfon acid, Acid catalysts, such as an alkyl sulfuric acid, an aluminum sulfate, lithium fluoride, potassium chloride, Metal salts, such as a cesium chloride, a calcium chloride, ferric chloride, and an aluminium phosphate, ZnO₂ / C and SnO, and SiO₂- metallic oxides, such as TiO₂, ZnO, Fe₂O₃, and a heteropolyacid, -- Alumina-alkali multicomputer systems, such as aluminum₂O₃-KOH-LiOH and aluminum₂O₃-NaOH, Nature, such as a mordenite and a ** cation-ized Y zeolite, and a composite zeolite, Organic metals, such as ion exchange resin, such as solid-state superacid, such as SO₄²⁻/ZnO₂ and SO₄²⁻/TiO₂, a cation exchange resin, and an anion exchange resin, tetrapod alkyl titanate and its polymer, Bu₂Sn(OBu) alumnus (OBu)₂, and the oxalic acid 1st tin, etc. are illustrated.

[0018] Especially as after treatment after an esterification reaction conclusion, although not limited, superfluous alcohol is distilled out of the inside of a system, for example, it passes through a saturation rinsing process, and the method of finally refining ester is mentioned. Moreover, it is also possible to use for the ester which does not refine, only distills off superfluous alcohol out of a system, and starts this invention especially.

[0019] It is the general term of the polymer which the polypropylene regin concerning this invention consists of considering a propylene component as a monomer unit, and the manufacture technique by difference of isotactic one, syndiotactic, the stereochemistry structure that is atactic and is classified, and a catalyst and a process does not ask.

[0020] The polypropylene regin concerning this invention is the general term of the polymer which makes a propylene an indispensable monomer, and, specifically, the copolymer with the homopolymer of a propylene, a propylene, ethylene, and/or 1-alkene (for example, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene, and such mixture) of carbon numbers 4-20, the copolymer of a propylene and styrene, etc. are illustrated. What ** of a random copolymer and a block copolymer is also contained in the above-mentioned copolymer.

[0021] the elastomer which has the blend or alloy structure which serves as the polyolefine system thermoplastic elastomer concerning this invention from EPDM or isobutylene isoprene rubber as polyethylene, polypropylene, and an elasticity phase as a hard phase -- further -- a hard phase ***** -- a transformer -1 -- syndiotactic [***** / 4---poly-/ and] -1, 2-polybutadiene and crystal polyethylene, the homopolymer system elastomer that consists of amorphous poly-******, and an amorphous polybutadiene and a chlorinated polyethylene as an elasticity phase are mentioned

[0022] the fraction which adds organic peroxide etc. in ***** of olefin system rubber, the blended type by simple mechanical blend of polyolefin resin and olefin system rubber, and polyolefin resin, is made to carry out partial bridge formation of the rubber phase, and is obtained as polyolefine system thermoplastic elastomer concerning this invention -- bridge formation -- a blended type and polypropylene -- a continuous phase and bridge formation -- it consists of the complex which uses EPDM as a dispersed phase -- perfect -- bridge formation -- there is a blended type etc. and it is not based on the

type or the manipulation technique of these

[0023] It is also possible to carry out the polymer blend of other resins to the above, a polypropylene resin, polyolefine system thermoplastic elastomer, or those mixture, to alloy-ize them into them, and to use them for them.

[0024] As an example of the above-mentioned polymer which can carry out a blend Natural rubber, styrene-butadiene rubber, butadiene rubber, polyisoprene rubber, An ethylene propylene diene terpolymer, nitril butadiene rubber, Rubber-like polymers, such as chloroprene rubber, isobutylene isoprene rubber, polyurethane rubber, and silicone rubber, Nylon 6, Nylon 66, Nylon 610, Nylon 612, Nylon 11, Nylon 12, copolymerization nylon, Amide system polymers, such as nylon MXD6 and denaturation polyamide 6T, a polyethylene terephthalate, A polybutylene terephthalate, polyhexamethylene terephthalate, Ester system polymers, such as polyethylene isophthalate, polytetramethylene sebacate, and a polypropylene horse mackerel peat, Polyethylene, the Poly 4-methyl pentene -1, a polyvinyl chloride, a polyvinylidene chloride, ABS plastics, polystyrene, an AS resin, methacrylic resin, polyvinyl alcohol, ethylene vinyl acetate, a cellulose plastic, etc. are mentioned.

[0025] Furthermore, the polystyrene system thermoplastic elastomer represented by polystyrene/polybutadiene, PVC system thermoplastic elastomer represented by a crystal polyvinyl chloride / NBR, The thermoplastic elastomer polyester represented by polyester/polyether, The polyurethane system thermoplastic elastomer represented by urethane structure / polyester, The polyamide system elastomer represented by a polyamide/polyester, It is possible to also blend the elastic elastomer by which the account of an example is carried out by the fluorine polymer system elastomer represented by a fluororesin/fluororubber, the ionomer system thermoplastic elastomer represented by a metal carboxy rate ion cluster / amorphous polyethylene.

[0026] although the loadings of this ester can be variously chosen according to the combination purpose -- usually -- this resinous principle 100 weight section -- receiving -- 0.2 - 60 weight section grade -- it is 0.2 - 35 weight section grade preferably Generally, even if the predetermined reforming effect is hard to be acquired and it blends conversely exceeding the concerned loadings, as for increase of a remarkable effect, it carries out and is not desirable at under the above-mentioned loadings that cannot expect but bleeding increases on the contrary etc.

[0027] The example of a recommendation of the concerned loadings according to the key objective is shown below. That is, in flexibility, cold resistance, and elasticity combination aiming at a shock-proof improvement, it is 0.2 - 5 weight section grade in hard combination aiming at enhancement 5 - 60 weight section grade, workability, fluid, and shock-proof.

[0028] Moreover, in the system which blended bulking agents, such as a calcium carbonate, a fiberglass mat, titanium oxide, clay, carbon black, an antimony oxide, hydration aluminum, a magnesia, a calcium hydroxide, silicic acid, and a metal powder, the loadings about 1 - 100 weight section are chosen.

[0029] Conventionally, this ester may be used together with various kinds of ester compounds known as a plasticizer and a lubricant, and may be blended with the concerned polypropylene resin or polyolefine system thermoplastic elastomer, and those mixture. such a plasticizer ***** -- benzoates, such as ethylene glycol dibenzoate and propylene glycol dibenzoate, dibutyl phthalate, a phthalic-acid dihexyl, ***** (2-ethylhexyl), ***** (n-octyl), a phthalic acid diisononyl ester, a diisodecyl phthalate, phthalic-acid ***** , a phthalic acid ditridecyl ester, and gold [a diamond / 79] -- said -- the phthalic ester of 911, and ***** 79 -- said -- phthalic esters, such as a phthalic ester of 911, a phthalic-acid dibutoxy ethyl, and a phthalic acid benzyl butyl ester, and [0030] Aliphatic system ester, such as ***** (2-ethylhexyl), ***** (n-octyl), diisononyl adipate, a diisodecyl adipate, the adipate of ***** 610, an adipate of gold ones 79 a diamond, an adipate of ***** 79, an adipic-acid dibutoxy ethyl, a dioctyl azelate, and *****

(2-ethylhexyl), [0031] Trimellitic acid ester, such as trimellitic acid **** (2-ethylhexyl), trimellitic acid **** (n-octyl), a trimellitic acid ***** nonyl, trimellitic acid triisodecyl, trimellitic acid ester of gold one 79 a diamond, trimellitic acid ester of ***** 79, and a trimellitic acid ***** ethyl, [0032] Phosphoric ester, such as tricresyl phosphate, a phosphoric-acid-2-ethylhexyl diphenyl, and a phosphoric-acid ***** ethyl, [0033] Polyester system plasticizers, such as a propylene glycol and an adipic-acid system, a propylene glycol and a phthalic-acid system, a butylene glycol and an adipic-acid system, and a propylene glycol, a sebacic-acid system, [0034] Epoxy system plasticizers, such as epoxidation soybean-oil, epoxidation linseed-oil, epoxy stearin acid octyl, 4, 5-epoxy hexahydrophthalic acid dioctyl, 4, and 5-epoxy hexahydrophthalic acid screw (9, 10-epoxy stearyl), chlorinated paraffin, etc. are illustrated.

[0035] As such a lubricant, the fatty acid ester of polyhydric alcohol, such as aliphatic system ester, such as a butyl stearate, a stearin acid octyl, stearin acid tridecyl, a lauric-acid octyl, and oleic-acid oleyl, a pentaerythritol tetrapod ***** rate, a pentaerythritol ***** pli rate, a trimethylol-propane ***** pli rate, and trimethylol-propane trio ***** , is illustrated.

[0036] Although the loadings of the above-mentioned plasticizer used together by request and a lubricant are not limited especially as long as a predetermined effect is acquired, they are usually 1 - 30 weight section grade to a polypropylene resin or polyolefine system thermoplastic elastomer, and those mixture 100 weight sections.

[0037] Various additives, such as a stabilizer, a stabilization assistant, a workability enhancement resin, an ultraviolet ray absorbent, an antioxidant, a nucleating additive, a bulking agent, a coloring agent, a foaming agent, a lubricant, a resin reinforcement, a cross linking agent, an antimicrobial agent, an antifungal agent, a flame retarder, a mold releasing agent, an insecticide, a repellent, a plate-out inhibitor, and an antistatic agent, etc. can be blended with the polyolefine system resin constituent concerning this invention if needed.

[0038] Especially the manipulation technique of the polyolefine system resin constituent concerning this invention is not limited. For example, the technique of obtaining a product, and the technique of supplying and fabricating the concerned resin constituent to a direct making machine are possible by letting the polyolefine system resin constituent which carried out preliminary mulling of the additive blended this resinous principle, this ester, and if needed, and obtained it pass to various

making machines.

[0039] The reserve mixing of a polyolefine system resin constituent is prepared by mulling the various components of the specified quantity using conventionally well-known kneading machines, such as a Banbury mixer, a Henschel mixer, and a ribbon blender, and the addition sequence is not asked.

[0040] The polyolefine system resin constituent obtained in this way Calender molding, extrusion molding, injection molding, a paste technique, an extension manipulation, a spinning manipulation, etc., It is conventionally fabricated by the technique used in each field. An automobile, Films, such as individual packing of industrial parts fields, such as a homeuse-electronics product, containers, miscellaneous goods, and snack confectionery, an instant food and tobacco, The flat yarns for textiles of a carpet, such as contest the deflection [a base fabric and] made from PP, the monofilament of a rope or a fishing net, Engineering works and construction fields, such as a lagging material of a tarpaulin, ***** , a structural gasket, and a makeup steel plate, It is useful as the elasticity applied to hose tubes, such as a duct hose flexible tube, a leather, the materials for agriculture, packing, an electrical-wire cable, various joint material, cold storage parts, the flexible grant agent of concrete, a porous film, etc., half-hard, and a hard constituent.

[0041] Especially, it is useful as a material of the automobile which is the intended use of thermoplastic elastomer and vehicle parts, household-electric-appliances parts, electrical wire and a hose tube, and engineering works, construction and building materials.

[0042]

[Example] An example is hung up over below and this invention is explained to it in detail. In addition, the property of the resin constituent in each example was measured by the following technique, and was evaluated.

[0043] The manufacture:polypropylene resin of a test piece and predetermined ester are mixed at 220 degrees C using a lab plastic strike mill, and a polyolefine system resin constituent is obtained.

[0044] Next, a sheet with a thickness of about 1mm is created under a preheating (3 minutes) and the condition of pressurization (2 minutes, 100kg/cm²) using the 30t press which carried out the temperature up to 220 degrees C. The obtained sheet is cut out in a predetermined size and each examination is presented.

[0045] Measurement:model of melt flow rate (MFR) : Shimazu Flow tester CFT-500C test temperature : 200 degree-C cylinder pressure:10.0kgf/cm² die : L 10.0mm D 1.0mm preheating time : 240s [0046] Bleeding [-proof] Nature: After leaving a press sheet for one week under a room temperature, the existence of bleeding was observed visually and the following three-stages estimated.

When there is no bleeding When O bleeding occurs slightly In a certain case, O bleeding is notably. x [0047] Tension-test: Based on JIS K 6723, the tension test was performed in 25 degrees C, and plasticizing efficiency was evaluated by measuring fracture elongation.

[0048] : [Cold-resistant] The softening temperature of crash ***** was measured based on JIS K 6745.

[0049] To the [homopolymer:tradename "PN-150" and Tokuyama Soda Co., Ltd. make] made from example 1 polypropylene 100 weight section, hexahydrophthalic acid ***** nonyl 5 weight section combination was carried out, and the press sheet was prepared. When MFR of the obtained sheet was measured, they were 13g / 10 minutes.

[0050] As two examples ester, ***** (n-*****) was used, and also the sheet was prepared according to the example 1. When MFR of the obtained sheet was measured, they were 13g / 10 minutes.

[0051] As three examples ester, hexahydrophthalic acid ***** was used, and also the sheet was prepared according to the example 1. When MFR of the obtained sheet was measured, they were 12g / 10 minutes.

[0052] As four examples ester, hexahydrophthalic acid dioleoyl was used, and also the sheet was prepared according to the example 1. When MFR of the obtained sheet was measured, they were 12g / 10 minutes.

[0053] As five examples ester, 4-methyl hexahydrophthalic acid ***** nonyl was used, and also the sheet was prepared according to the example 1. When MFR of the obtained sheet was measured, they were 13g / 10 minutes.

[0054] As six examples ester, the tetrahydrophthalic acid ***** nonyl was used, and also sheet physical properties were prepared according to the example 1. When MFR of the obtained sheet was measured, they were 13g / 10 minutes.

[0055] As seven examples ester, tetrahydrophthalic acid ***** was used, and also sheet physical properties were prepared according to the example 1. When MFR of the obtained sheet was measured, they were 13g / 10 minutes.

[0056] As eight examples ester, tetrahydrophthalic acid ** (2-hexyl *****) was used, and also the sheet was prepared according to the example 1. When MFR of the obtained sheet was measured, they were 12g / 10 minutes.

[0057] As nine examples ester, 4-methyl tetrahydrophthalic acid ***** nonyl was used, and also the sheet was prepared according to the example 1. When MFR of the obtained sheet was measured, they were 13g / 10 minutes.

[0058] As ten examples ester, 3 and 6- and the methylene tetrahydrophthalic acid ***** nonyl were used, and also the sheet was prepared according to the example 1. When MFR of the obtained sheet was measured, they were 13g / 10 minutes.

[0059] An example of comparison 1 ester system compound was not blended, and also the sheet was prepared according to the example 1. When MFR of the obtained sheet was measured, they were 9g / 10 minutes.

[0060] After having carried out hexahydrophthalic acid ***** nonyl (it is written as "H-9" below.) 25 weight section combination and preparing a press sheet to the [block-copolymer:tradename "PN-630" and Tokuyama Soda Co., Ltd. make] made from example 11 polypropylene 100 weight section, the sheet physical properties were measured. The obtained result is shown in the 1st table.

[0061] As 12 examples ester, ***** (n-*****) (it is written as "H-10" below.) was used, and also sheet

physical properties were measured according to the example 11. The obtained result is shown in the 1st table.

[0062] As 13 examples ester, hexahydrophthalic acid ***** (it is written as "H-13" below.) was used, and also sheet physical properties were measured according to the example 11. The obtained result is shown in the 1st table.

[0063] As 14 examples ester, hexahydrophthalic acid dioleoyl (it is written as "H-18" below.) was used, and also sheet physical properties were measured according to the example 11. The obtained result is shown in the 1st table.

[0064] As 15 examples ester, 4-methyl hexahydrophthalic acid ***** nonyl (it is written as "MH-9" below.) was used, and also sheet physical properties were measured according to the example 11. The obtained result is shown in the 1st table.

[0065] As 16 examples ester, the tetrahydrophthalic acid ***** nonyl (it is written as "T-9" below.) was used, and also sheet physical properties were measured according to the example 11. The obtained result is shown in the 1st table.

[0066] As 17 examples ester, tetrahydrophthalic acid ***** (it is written as "T-11" below.) was used, and also sheet physical properties were measured according to the example 11. The obtained result is shown in the 1st table.

[0067] As 18 examples ester, tetrahydrophthalic acid ** (2-hexyl *****) (it is written as "T-16" below.) was used, and also sheet physical properties were measured according to the example 11. The obtained result is shown in the 1st table.

[0068] As 19 examples ester, 4-methyl tetrahydrophthalic acid ***** nonyl (it is written as "MT-9" below.) was used, and also sheet physical properties were measured according to the example 11. The obtained result is shown in the 1st table.

[0069] As 20 examples ester, 3 and 6- and the methylene tetrahydrophthalic acid ***** nonyl (it is written as "NA-9" below.) were used, and also sheet physical properties were measured according to the example 11. The obtained result is shown in the 1st table.

[0070] As two examples ester of a comparison, the liquid paraffin was used, and also sheet physical properties were measured according to the example 11. The obtained result is shown in the 1st table.

[0071] As three examples ester of a comparison, stearin acid tridecyl (it is written as "TDS" below.) was used, and also sheet physical properties were measured according to the example 11. The obtained result is shown in the 1st table.

[0072] As four examples ester of a comparison, ***** (2-ethylhexyl) (it is written as "DOP" below.) was used, and also sheet physical properties were measured according to the example 11. The obtained result is shown in the 1st table.

[0073] The press sheet of the polypropylene (block copolymer) which does not blend an example of comparison 5 ester system compound was prepared, and the sheet physical properties were measured according to the example 11. The obtained result is shown in the 1st table.

[Table 1]

第 1 表

	エステル	ブリード	伸 び (%)	柔軟温度 (℃)
実施例 1 1	H - 9	◎	3 3 0	- 4 2
実施例 1 2	H - 1 0	◎	3 1 4	- 4 6
実施例 1 3	H - 1 3	◎	2 8 0	- 4 0
実施例 1 4	H - 1 8	◎	2 4 1	- 4 0
実施例 1 5	M H - 9	◎	3 2 3	- 4 2
実施例 1 6	T - 9	◎	3 2 6	- 4 2
実施例 1 7	T - 1 1	◎	3 0 2	- 4 6
実施例 1 8	T - 1 6	◎	2 5 7	- 4 0
実施例 1 9	M T - 9	◎	3 2 0	- 4 2
実施例 2 0	N A - 9	◎	3 1 5	- 4 2
比較例 2	流動パラフィン	◎	2 2	- 3 5
比較例 3	T D S	○	3 1	- 3 3
比較例 4	D O P	×	1 4 4	- 3 8
比較例 5	-	-	7 5	1

[0074]

[Effect of the invention] By blending the ester system compound concerning this invention, it excels in a compatibility, plasticizing efficiency, cold resistance, shock resistance, and a fluidity, a fabricating operation can be easily done by the various molding technique by thermoplasticity, and a useful polyolefine system resin constituent can be obtained as a molding material.

[Translation done.]

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TECHNICAL FIELD

[Field of the Invention] this invention relates to a polyolefine system resin constituent useful as a molding material.

[0002] A polypropylene resin, polyolefine system thermoplastic elastomer, and those mixture are known as a material useful for various intended use, such as an injection-molding article, a film, a flat yarn, fiber, a blow-molding article, and an extrusion-molding article.

[0003] Since the shock resistance in low temperature and flexibility were low, the polypropylene resin had the inclination to receive a limit in the use especially in a cold district, and since the concerned resin had a low fluidity, when bulking agents, such as a flame retarder, and a calcium carbonate, a glass fiber, were blended and processed, it had the problem that a moldability was inferior.

[0004] Although polyolefine system thermoplastic elastomer has shock resistance and good flexibility, since a property like a polyvinyl chloride resin system elastomer or a soft polyvinylchloride resin is not provided, in spite of the room of an improvement having accepted, in addition, the improvement means effective until now is not especially known as a material in the intended use of inner sheathing, such as an automobile and a vehicle, electrical wire and a household-electric-appliances device, engineering works, construction and building materials, a hose tube, etc.

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EFFECT OF THE INVENTION

[Effect of the invention] By blending the ester system compound concerning this invention, it excels in a compatibility, plasticizing efficiency, cold resistance, shock resistance, and a fluidity, a fabricating operation can be easily done by the various molding technique by thermoplasticity, and a useful polyolefine system resin constituent can be obtained as a molding material.

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TECHNICAL PROBLEM

[Object of the Invention] The fluidity and the workability of a resin are improved and the shock resistance (cold resistance) in low temperature and flexibility aim this invention at offering a good polyolefine system resin constituent.

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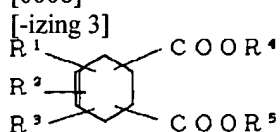
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MEANS

[The means for solving a technical problem] In order that this invention persons may attain the above-mentioned purpose, zealously, to a polypropylene resin, polyolefine system thermoplastic elastomer, or those mixture, by blending the ester compound which has specific structure, they find out that a desired effect is acquired and came to complete this invention based on such knowledge as a result of the study.

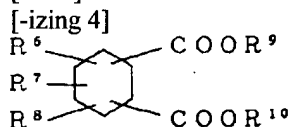
[0007] That is, it is characterized by the polyolefine system resin constituent concerning this invention coming to blend one sort expressed with a general formula (1) or a general formula (2), or two sorts or more of alicyclic dicarboxylic-acid ester (for it to be named "this ester" generically below.) to a polypropylene resin and/or polyolefine system thermoplastic elastomer (it being named "this resinous principle" generically below.).

[0008]



the inside of [formula, and R1, R2 and R3 -- an identity -- or -- differing -- a hydrogen atom, the shape of a straight chain of carbon numbers 1-5, a branched-chain alkyl group, the shape of a straight chain of carbon numbers 2-5, and a branched-chain alkenyl machine -- or -- and a methylene group is expressed R4 and R5 -- an identity -- or it differs and the shape of a straight chain, the branched-chain alkyl group, or alkenyl machine of carbon numbers 6-28 is expressed]

[0009]



the inside of [formula, and R6, R7 and R8 -- an identity -- or -- differing -- a hydrogen atom, the shape of a straight chain of carbon numbers 1-5, a branched-chain alkyl group, the shape of a straight chain of carbon numbers 2-5, and a branched-chain alkenyl machine -- or -- and a methylene group is expressed R9 and R10 -- an identity -- or it differs and the shape of a straight chain, the branched-chain alkyl group, or alkenyl machine of carbon numbers 6-28 is expressed]

[0010] Although especially the manufacture technique of this ester is not limited and well-known arbitrary operations can be conventionally used for it, the method of esterifying a predetermined dicarboxylic acid, or the acid anhydride and a predetermined fatty alcohol as the general technique, while removing produced water under presence of a non-catalyst or a catalyst is mentioned.

[0011] The ester expressed with a general formula (1) is easily compounded by carrying out the esterification reaction of an alicyclic unsaturation dicarboxylic acid, or its predetermined anhydride and predetermined fatty alcohol according to a conventional method.

[0012] As the concerned alicyclic unsaturation dicarboxylic acid or its anhydride, the acid anhydride obtained by the reaction of deca trien, such as a tetrahydrophthalic acid, a methyl tetrahydrophthalic acid, a dimethyl butenyl tetrahydrophthalic acid, a ***** acid, a methyl ***** acid, methyl highness *****s, those anhydrides and those isomers (a geometrical isomer and a structural isomer are included.), and *****s, alpha-terpinene, and a maleic anhydride, its disengagement carboxylic acid, etc. are illustrated.

[0013] The ester expressed with a general formula (2) is easily compounded by carrying out the esterification reaction of an alicyclic saturation dicarboxylic acid, or its predetermined acid anhydride and predetermined fatty alcohol according to a conventional method. Moreover, it can obtain also by carrying out nuclear hydrogenation of the ester expressed with a general formula (1).

[0014] As the concerned alicyclic saturation dicarboxylic acid or its anhydride, hexahydrophthalic acid, methyl hexahydrophthalic acid, ***** acid hydrogenation object, methyl ***** acid hydrogenation object, 1, and 4-cyclohexane dicarboxylic acids, these acid anhydrides, those isomers (a geometrical isomer is included.), etc. are illustrated.

[0015] The fatty alcohol used as an alcoholic component of each above-mentioned ester concerning this invention is a fatty alcohol of the saturation of carbon numbers 6-28, or an unsaturation, and is a fatty alcohol of carbon numbers 8-24 more preferably. Since the compatibility to a polyolefine system resin falls in less than six alcohol, and it is easy to carry out bleeding of the carbon number, and the molecular weight of ester becomes small and oil resistance falls in the alcohol in which a volatility-proof is inferior with alcohol and a carbon number exceeds 28 conversely, it is not desirable.

[0016] As a desirable fatty alcohol concerning this invention A heptanol, 2-ethyl hexanol, n-octanol, iso nonanol, A 3, 5, and 5-trimethyl hexanol, n-decanol, an iso decanol, An undeca Norian, a dodecanol, a tridecyl alcohol, ***** 610 (vista chemical Far East company make), ***** 79 -- said -- 911 (shell chemistry company make) and gold [a diamond / 79] -- said -- 911 -- said -- 11 -- said -- 113 (Mitsubishi Kasei Corp. make) -- The dimerization alcohol obtained by the gar bed reaction of a myristyl alcohol, cetyl alcohol, a stearyl alcohol, a behenyl alcohol, oleyl alcohol, and these alcohol is illustrated.

[0017] As an esterification catalyst chosen and applied in the above-mentioned esterification A sulfuric acid, a hydrochloric acid, a phosphoric acid, Para toluenesulfonic acid, a methanesulfon acid, Acid catalysts, such as an alkyl sulfuric acid, an aluminum sulfate, lithium fluoride, potassium chloride, Metal salts, such as a cesium chloride, a calcium chloride, ferric chloride, and an aluminium phosphate, ZnO₂ / C and SnO, and SiO₂- metallic oxides, such as TiO₂, ZnO, Fe₂O₃, and a heteropolyacid, -- Alumina-alkali multicomputer systems, such as aluminum₂O₃-KOH-LiOH and aluminum₂O₃-NaOH, Nature, such as a mordenite and a ** cation-ized Y zeolite, and a composite zeolite, Organic metals, such as ion exchange resin, such as solid-state superacid, such as SO₄²⁻/ZnO₂ and SO₄²⁻/TiO₂, a cation exchange resin, and an anion exchange resin, tetrapod alkyl titanate and its polymer, Bu₂Sn(OBu) alumnum (OBu)₂, and the oxalic acid 1st tin, etc. are illustrated.

[0018] Especially as after treatment after an esterification reaction conclusion, although not limited, superfluous alcohol is distilled out of the inside of a system, for example, it passes through a saturation rinsing process, and the method of finally refining ester is mentioned. Moreover, it is also possible to use for the ester which does not refine, only distills off superfluous alcohol out of a system, and starts this invention especially.

[0019] It is the general term of the polymer which the polypropylene regin concerning this invention consists of considering a propylene component as a monomer unit, and the manufacture technique by difference of isotactic one, syndiotactic, the stereochemistry structure that is atactic and is classified, and a catalyst and a process does not ask.

[0020] The polypropylene regin concerning this invention is the general term of the polymer which makes a propylene an indispensable monomer, and, specifically, the copolymer with the homopolymer of a propylene, a propylene, ethylene, and/or 1-alkene (for example, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene, and such mixture) of carbon numbers 4-20, the copolymer of a propylene and styrene, etc. are illustrated. What ** of a random copolymer and a block copolymer is also contained in the above-mentioned copolymer.

[0021] the elastomer which has the blend or alloy structure which serves as the polyolefine system thermoplastic elastomer concerning this invention from EPDM or isobutylene isoprene rubber as polyethylene, polypropylene, and an elasticity phase as a hard phase -- further -- a hard phase ***** -- a transformer -1 -- syndiotactic [***** / 4---poly-/ and] -1, 2-polybutadiene and crystal polyethylene, the homopolymer system elastomer that consists of amorphous poly-***** , and an amorphous polybutadiene and a chlorinated polyethylene as an elasticity phase are mentioned

[0022] the fraction which adds organic peroxide etc. in ***** of olefin system rubber, the blended type by simple mechanical blend of polyolefin resin and olefin system rubber, and polyolefin resin, is made to carry out partial bridge formation of the rubber phase, and is obtained as polyolefine system thermoplastic elastomer concerning this invention -- bridge formation -- a blended type and polypropylene -- a continuous phase and bridge formation -- it consists of the complex which uses EPDM as a dispersed phase -- perfect -- bridge formation -- there is a blended type etc. and it is not based on the type or the manipulation technique of these

[0023] It is also possible to carry out the polymer blend of other resins to the above, a polypropylene regin, polyolefine system thermoplastic elastomer, or those mixture, to alloy-ize them into them, and to use them for them.

[0024] As an example of the above-mentioned polymer which can carry out a blend Natural rubber, styrene-butadiene rubber, butadiene rubber, polyisoprene rubber, An ethylene propylene diene terpolymer, nitril butadiene rubber, Rubber-like polymers, such as chloroprene rubber, isobutylene isoprene rubber, polyurethane rubber, and silicone rubber, Nylon 6, Nylon 66, Nylon 610, Nylon 612, Nylon 11, Nylon 12, copolymerization nylon, Amide system polymers, such as nylon MXD6 and denaturation polyamide 6T, a polyethylene terephthalate, A polybutylene terephthalate, polyhexamethylene terephthalate, Ester system polymers, such as polyethylene isophthalate, polytetramethylene sebacate, and a polypropylene horse mackerel peat, Polyethylene, the Polly 4-methyl pentene -1, a polyvinyl chloride, a polyvinylidene chloride, ABS plastics, polystyrene, an AS resin, methacrylic resin, polyvinyl alcohol, ethylene vinyl acetate, a cellulose plastic, etc. are mentioned.

[0025] Furthermore, the polystyrene system thermoplastic elastomer represented by polystyrene/polybutadiene, PVC system thermoplastic elastomer represented by a crystal polyvinyl chloride / NBR, The thermoplastic elastomer polyester represented by polyester/polyether, The polyurethane system thermoplastic elastomer represented by urethane structure / polyester, The polyamide system elastomer represented by a polyamide/polyester, It is possible to also blend the elastic elastomer by which the account of an example is carried out by the fluorine polymer system elastomer represented by a fluororesin/fluororubber, the ionomer system thermoplastic elastomer represented by a metal carboxy rate ion cluster / amorphous polyethylene.

[0026] although the loadings of this ester can be variously chosen according to the combination purpose -- usually -- this resinous principle 100 weight section -- receiving -- 0.2 - 60 weight section grade -- it is 0.2 - 35 weight section grade

preferably Generally, even if the predetermined reforming effect is hard to be acquired and it blends conversely exceeding the concerned loadings, as for increase of a remarkable effect, it carries out and is not desirable at under the above-mentioned loadings that cannot expect but bleeding increases on the contrary etc.

[0027] The example of a recommendation of the concerned loadings according to the key objective is shown below. That is, in flexibility, cold resistance, and elasticity combination aiming at a shock-proof improvement, it is 0.2 - 5 weight section grade in hard combination aiming at enhancement 5 - 60 weight section grade, workability, fluid, and shock-proof.

[0028] Moreover, in the system which blended bulking agents, such as a calcium carbonate, a fiberglass mat, titanium oxide, clay, carbon black, an antimony oxide, hydration aluminum, a magnesia, a calcium hydroxide, silicic acid, and a metal powder, the loadings about 1 - 100 weight section are chosen.

[0029] Conventionally, this ester may be used together with various kinds of ester compounds known as a plasticizer and a lubricant, and may be blended with the concerned polypropylene resin or polyolefine system thermoplastic elastomer, and those mixture. such a plasticizer ***** -- benzoates, such as ethylene glycol dibenzoate and propylene glycol dibenzoate, dibutyl phthalate, a phthalic-acid dihexyl, ***** (2-ethylhexyl), ***** (n-octyl), a phthalic acid diisononyl ester, a diisodecyl phthalate, phthalic-acid ***** , a phthalic acid dtridecyl ester, and gold [a diamond / 79] -- said -- the phthalic ester of 911, and ***** 79 -- said -- phthalic esters, such as a phthalic ester of 911, a phthalic-acid dibutoxy ethyl, and a phthalic acid benzyl butyl ester, and [0030] Aliphatic system ester, such as ***** (2-ethylhexyl), ***** (n-octyl), diisononyl adipate, a diisodecyl adipate, the adipate of ***** 610, an adipate of gold ones 79 a diamond, an adipate of ***** 79, an adipic-acid dibutoxy ethyl, a dioctyl azelate, and ***** (2-ethylhexyl), [0031] Trimellitic acid ester, such as trimellitic acid **** (2-ethylhexyl), trimellitic acid **** (n-octyl), a trimellitic acid ***** nonyl, trimellitic acid triisodecyl, trimellitic acid ester of gold one 79 a diamond, trimellitic acid ester of ***** 79, and a trimellitic acid ***** ethyl, [0032] Phosphoric ester, such as tricresyl phosphate, a phosphoric-acid-2-ethylhexyl diphenyl, and a phosphoric-acid ***** ethyl, [0033] Polyester system plasticizers, such as a propylene glycol and an adipic-acid system, a propylene glycol and a phthalic-acid system, a butylene glycol and an adipic-acid system, and a propylene glycol, a sebacic-acid system, [0034] Epoxy system plasticizers, such as epoxidation soybean-oil, epoxidation linseed-oil, epoxy stearin acid octyl, 4, 5-epoxy hexahydrophthalic acid dioctyl, 4, and 5-epoxy hexahydrophthalic acid screw (9, 10-epoxy stearyl), chlorinated paraffin, etc. are illustrated.

[0035] As such a lubricant, the fatty acid ester of polyhydric alcohol, such as aliphatic system ester, such as a butyl stearate, a stearin acid octyl, stearin acid tridecyl, a lauric-acid octyl, and oleic-acid oleyl, a pentaerythritol tetrapod ***** rate, a pentaerythritol ***** pli rate, a trimethylol-propane ***** pli rate, and trimethylol-propane trio ***** , is illustrated.

[0036] Although the loadings of the above-mentioned plasticizer used together by request and a lubricant are not limited especially as long as a predetermined effect is acquired, they are usually 1 - 30 weight section grade to a polypropylene resin or polyolefine system thermoplastic elastomer, and those mixture 100 weight sections.

[0037] Various additives, such as a stabilizer, a stabilization assistant, a workability enhancement resin, an ultraviolet ray absorbent, an antioxidant, a nucleating additive, a bulking agent, a coloring agent, a foaming agent, a lubricant, a resin reinforcement, a cross linking agent, an antimicrobial agent, an antifungal agent, a flame retarder, a mold releasing agent, an insecticide, a repellent, a plate-out inhibitor, and an antistatic agent, etc. can be blended with the polyolefine system resin constituent concerning this invention if needed.

[0038] Especially the manipulation technique of the polyolefine system resin constituent concerning this invention is not limited. For example, the technique of obtaining a product, and the technique of supplying and fabricating the concerned resin constituent to a direct making machine are possible by letting the polyolefine system resin constituent which carried out preliminary mulling of the additive blended this resinous principle, this ester, and if needed, and obtained it pass to various making machines.

[0039] The reserve mixing of a polyolefine system resin constituent is prepared by mulling the various components of the specified quantity using conventionally well-known kneading machines, such as a Banbury mixer, a Henschel mixer, and a ribbon blender, and the addition sequence is not asked.

[0040] The polyolefine system resin constituent obtained in this way Calender molding, extrusion molding, injection molding, a paste technique, an extension manipulation, a spinning manipulation, etc., It is conventionally fabricated by the technique used in each field. An automobile, Films, such as individual packing of industrial parts fields, such as a home-use-electronics product, containers, miscellaneous goods, and snack confectionery, an instant food and tobacco, The flat yarns for textiles of a carpet, such as contest the deflection [a base fabric and] made from PP, the monofilament of a rope or a fishing net, Engineering works and construction fields, such as a lagging material of a tarpaulin, ***** , a structural gasket, and a makeup steel plate, It is useful as the elasticity applied to hose tubes, such as a duct hose flexible tube, a leather, the materials for agriculture, packing, an electrical-wire cable, various joint material, cold storage parts, the flexible grant agent of concrete, a porous film, etc., half-hard, and a hard constituent.

[0041] Especially, it is useful as a material of the automobile which is the intended use of thermoplastic elastomer and vehicle parts, household-electric-appliances parts, electrical wire and a hose tube, and engineering works, construction and building materials.

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EXAMPLE

[Example] An example is hung up over below and this invention is explained to it in detail. In addition, the property of the resin constituent in each example was measured by the following technique, and was evaluated.

[0043] The manufacture: polypropylene resin of a test piece and predetermined ester are mixed at 220 degrees C using a lab plastic strike mill, and a polyolefine system resin constituent is obtained.

[0044] Next, a sheet with a thickness of about 1mm is created under a preheating (3 minutes) and the condition of pressurization (2 minutes, 100kg/cm²) using the 30t press which carried out the temperature up to 220 degrees C. The obtained sheet is cut out in a predetermined size and each examination is presented.

[0045] Measurement: model of melt flow rate (MFR) : Shimazu Flow tester CFT-500C test temperature : 200 degree-C cylinder pressure: 10.0kgf/cm² die : L 10.0mm D 1.0mm preheating time : 240s [0046] Bleeding [-proof] Nature: After leaving a press sheet for one week under a room temperature, the existence of bleeding was observed visually and the following three-stages estimated.

When there is no bleeding When O bleeding occurs slightly In a certain case, O bleeding is notably. x [0047] Tension-test: Based on JIS K 6723, the tension test was performed in 25 degrees C, and plasticizing efficiency was evaluated by measuring fracture elongation.

[0048] : [Cold-resistant] The softening temperature of crash ***** was measured based on JIS K 6745.

[0049] To the [homopolymer: tradename "PN-150" and Tokuyama Soda Co., Ltd. make] made from example 1 polypropylene 100 weight section, hexahydrophthalic acid ***** nonyl 5 weight section combination was carried out, and the press sheet was prepared. When MFR of the obtained sheet was measured, they were 13g / 10 minutes.

[0050] As two examples ester, ***** (n-*****) was used, and also the sheet was prepared according to the example 1. When MFR of the obtained sheet was measured, they were 13g / 10 minutes.

[0051] As three examples ester, hexahydrophthalic acid ***** was used, and also the sheet was prepared according to the example 1. When MFR of the obtained sheet was measured, they were 12g / 10 minutes.

[0052] As four examples ester, hexahydrophthalic acid dioleoyl was used, and also the sheet was prepared according to the example 1. When MFR of the obtained sheet was measured, they were 12g / 10 minutes.

[0053] As five examples ester, 4-methyl hexahydrophthalic acid ***** nonyl was used, and also the sheet was prepared according to the example 1. When MFR of the obtained sheet was measured, they were 13g / 10 minutes.

[0054] As six examples ester, the tetrahydrophthalic acid ***** nonyl was used, and also sheet physical properties were prepared according to the example 1. When MFR of the obtained sheet was measured, they were 13g / 10 minutes.

[0055] As seven examples ester, tetrahydrophthalic acid ***** was used, and also sheet physical properties were prepared according to the example 1. When MFR of the obtained sheet was measured, they were 13g / 10 minutes.

[0056] As eight examples ester, tetrahydrophthalic acid ** (2-hexyl *****) was used, and also the sheet was prepared according to the example 1. When MFR of the obtained sheet was measured, they were 12g / 10 minutes.

[0057] As nine examples ester, 4-methyl tetrahydrophthalic acid ***** nonyl was used, and also the sheet was prepared according to the example 1. When MFR of the obtained sheet was measured, they were 13g / 10 minutes.

[0058] As ten examples ester, 3 and 6- and the methylene tetrahydrophthalic acid ***** nonyl were used, and also the sheet was prepared according to the example 1. When MFR of the obtained sheet was measured, they were 13g / 10 minutes.

[0059] An example of comparison 1 ester system compound was not blended, and also the sheet was prepared according to the example 1. When MFR of the obtained sheet was measured, they were 9g / 10 minutes.

[0060] After having carried out hexahydrophthalic acid ***** nonyl (it is written as "H-9" below.) 25 weight section combination and preparing a press sheet to the [block-copolymer: tradename "PN-630" and Tokuyama Soda Co., Ltd. make] made from example 11 polypropylene 100 weight section, the sheet physical properties were measured. The obtained result is shown in the 1st table.

[0061] As 12 examples ester, ***** (n-*****) (it is written as "H-10" below.) was used, and also sheet physical properties were measured according to the example 11. The obtained result is shown in the 1st table.

[0062] As 13 examples ester, hexahydrophthalic acid ***** (it is written as "H-13" below.) was used, and also sheet physical properties were measured according to the example 11. The obtained result is shown in the 1st table.

[0063] As 14 examples ester, hexahydrophthalic acid dioleoyl (it is written as "H-18" below.) was used, and also sheet physical properties were measured according to the example 11. The obtained result is shown in the 1st table.

[0064] As 15 examples ester, 4-methyl hexahydrophthalic acid ***** nonyl (it is written as "MH-9" below.) was used, and also sheet physical properties were measured according to the example 11. The obtained result is shown in the 1st table.

[0065] As 16 examples ester, the tetrahydrophthal acid ***** nonyl (it is written as "T-9" below.) was used, and also sheet physical properties were measured according to the example 11. The obtained result is shown in the 1st table.

[0066] As 17 examples ester, tetrahydrophthal acid ***** (it is written as "T-11" below.) was used, and also sheet physical properties were measured according to the example 11. The obtained result is shown in the 1st table.

[0067] As 18 examples ester, tetrahydrophthal acid ** (2-hexyl *****) (it is written as "T-16" below.) was used, and also sheet physical properties were measured according to the example 11. The obtained result is shown in the 1st table.

[0068] As 19 examples ester, 4-methyl tetrahydrophthal acid ***** nonyl (it is written as "MT-9" below.) was used, and also sheet physical properties were measured according to the example 11. The obtained result is shown in the 1st table.

[0069] As 20 examples ester, 3 and 6- and the methylene tetrahydrophthal acid ***** nonyl (it is written as "NA-9" below.) were used, and also sheet physical properties were measured according to the example 11. The obtained result is shown in the 1st table.

[0070] As two examples ester of a comparison, the liquid paraffin was used, and also sheet physical properties were measured according to the example 11. The obtained result is shown in the 1st table.

[0071] As three examples ester of a comparison, stearin acid tridecyl (it is written as "TDS" below.) was used, and also sheet physical properties were measured according to the example 11. The obtained result is shown in the 1st table.

[0072] As four examples ester of a comparison, ***** (2-ethylhexyl) (it is written as "DOP" below.) was used, and also sheet physical properties were measured according to the example 11. The obtained result is shown in the 1st table.

[0073] The press sheet of the polypropylene (block copolymer) which does not blend an example of comparison 5 ester system compound was prepared, and the sheet physical properties were measured according to the example 11. The obtained result is shown in the 1st table.

[Table 1]

第 1 表

	エステル	ブリード	伸 び (%)	柔軟温度 (℃)
実施例 1 1	H-9	◎	330	-42
実施例 1 2	H-10	◎	314	-46
実施例 1 3	H-13	◎	280	-40
実施例 1 4	H-18	◎	241	-40
実施例 1 5	MH-9	◎	323	-42
実施例 1 6	T-9	◎	326	-42
実施例 1 7	T-11	◎	302	-46
実施例 1 8	T-16	◎	257	-40
実施例 1 9	MT-9	◎	320	-42
実施例 2 0	NA-9	◎	315	-42
比較例 2	流動パラフィン	◎	22	-35
比較例 3	TDS	○	31	-33
比較例 4	DOP	×	144	-38
比較例 5	-	-	75	1

[Translation done.]